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Attorney's Docket No. 022701-803

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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| In re Patent Application of | ) | |
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| Stefan BREUNIG et al | ) | Group Art Unit: 1712 |
| | ) | |
| Application No.: 09/202,244 | ) | Examiner: M. Moore |
| | ) | |
| Filed: February 19, 1999 | ) | |
| | ) | |
| For: METHOD FOR PREPARING SILICONE OILS BY HYDROSILYLATION WITH POLYORGANOHYDROGENOSILOXANES AND UNITS CONTAINING AT LEAST ONE HYDROCARBON RING INCLUDING AN OXYGEN ATOM, IN THE PRESENCE OF A HETEROGENEOUS CATALYTIC COMPOSITION | ) | |



**DECLARATION PURSUANT TO 37 C.F.R. § 1.132**

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

I, Gérard Mignani, declare:

(1) That I am a French citizen residing at Lyon (France).

(2) That I have been awarded a PhD in Chemisrty from the University of Rennes.

(3) That I am currently employed as Principal Scientist of the Chemical Section in the laboratories of Rhodia Silicones where I am responsible for handling and developping products and processes in the silicone field.

(4) That I have read and am familiar with the above-identified United States patent application filed on February 19, 1999, relating to a method for preparing

silicone oils by hydrosilylation with polyorganohydrogenosiloxanes and units containing at least one hydrocarbon ring including an oxygen atom in the presence of a heterogeneous catalytic composition. That, based thereon, I understand that the Examiner has concluded that *Jachmann et al* (U.S. Patent No. 5,187,251) teaches a reaction between a polyorganohydrosiloxane and an epoxy-containing compound for the preparation of a silicone oil as presently claimed. In accordance with my review of the file history, I respectfully disagree.

(5) In my expert opinion, one skilled in the art would reasonably conclude, based on the information contained in the as-filed disclosure, that the polyorganohydrosiloxane of the present invention and the catalytic composition of the present invention are different from the starting materials of *Jachmann et al* and due to this difference the hydrosilation reaction of the present invention leads to the production of a silicone that has a stable viscosity and low turbidity. In particular, the polyorgonohydrosiloxane synthesized in the present invention contains only SiH groups and is reacted with a heterogenous catalytic composition which would virtually eliminate the metal found in the final epoxy silicone product. Thus, the final silicone structure synthesized has a high level of epoxy function, low coloring, non-turbidity and stable viscosity. In contrast, the polyorgonohydrosiloxane synthesized by *Jachmann et al* is contains both SiH and epoxy groups, and the catalytic composition is not necessarily heterogeneous. Accordingly, it cannot be asserted that the properties

of the silicone product obtain by *Jachmann et al* are the same as the ones of the present invention.

(6) That, in an effort to overcome the outstanding rejections, however, I provide the following additional experimental data in support of the claimed invention. In my opinion, these additional experiments further confirm that the process for the preparation of functionalized silicon oils provides evidence of non-obviousness since the product has low coloring, non-turbidity and a stable viscosity.

Experiment 1:

6.07 $\mu$l of Karstedt homogeneous catalytic composition comprising 11.6% Pt (11.6 ppm of Pt in the mixture) and 8.68 g (69.89 mmol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

This mixture is heated to 90°C. 52 g (66.56 mmol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 1 hour.

After the reactant has been run in, the degree of conversion of SiH is 99.7%.

After devolatilization at 90°C for 2 hours, a functionalized oil is recovered which has a viscosity of 930 mPa.s.

The coloring of the oil is 240 hazen units and the platinum content is 11.6 ppm.

The level of epoxy quantitatively determined/theoretical epoxy level ratio is 0.91.

Experiment 2:

6.07 $\mu$l of Karstedt homogeneous catalytic composition comprising 11.6% Pt (11.6 ppm of Pt in the mixture) and 8.68 g (69.89 mmol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 52 g (66.56 mmol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 1 hour.

After the reactant has been run in, the degree of conversion of SiH is 99.7%.

Heating is continued for 3 hours. After filtration, the oil is devolatilized at 120°C for 2 hours.

The functionalized oil obtained is crosslinked and exists in solid form.

Experiment 3:

175 mg of milled heterogeneous catalyst comprising 1% Pt on a support composed of $TiO_2$, 16.7 g of toluene and 2.5 g (20.2 mmol) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 15 g of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion is 91.7%. 2 hours later, the degree is 96.6% and then reaches 97.4% 20 hours after the reactant has been run in.

The reaction mixture is filtered on a Eurofiltec R3506 filter under a pressure of $3.5 \times 10^5$ Pa.

The oil obtained is then devolatilized using a rotary evaporator at 100°C under a vacuum of $2 \times 10^2$ Pa.

A functionalized oil is recovered which is highly colored, of the order of 2430 hazen units, which has a platinum content of 8.1 ppm and which has a viscosity of 1460 mPa.s. The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.91.

Experiment 4:

3.89 g of non-milled heterogeneous catalytic composition of CAL 101 type (100 ppm of Pt in the mixture) and 16.7 g (0.134 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 250 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum,

The mixture is heated to 90°C. 100 g (0.128 mol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 98.6%. 2 hours after the reactant has been run in, the degree of conversion is 100%.

The reaction mass is filtered through sintered glass with a clarcel precoat. Devolatilization is carried out using a rotary evaporator at 100°C under a vacuum of 2 x $10^2$ Pa for 2 hours.

A perfectly transparent functionalized oil is recovered (coloring of the order of 83 hazen units and no turbidity). The viscosity measured is 290 mPa.s. and the platinum content is 2.1 ppm. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.96.

Experiment 5:

4.668 g of heterogeneous catalytic composition comprising 2.5% Pt on a CECA 2S support (100 ppm of Pt) and 166.9 g (1.344 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 2 liter three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 1 kg (1.28 mol) of polyorganohydrosiloxane of formula (XVIII) is run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 96.4% and this reaches 97.5% after 2 hours and then 99.7% after 5 hours,

After filtration, devolatilization is carried out using a rotary evaporator at 100°C under a vacuum of 2 x $10^2$ Pa.

I A functionalized oil is recovered which has a viscosity of 300 mPa.s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The coloring is 45 hazen units and the platinum content is less than 0.16 ppm. The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.96. No turbidity observed.

Experiment 6:

All the washed, dried and recovered heterogeneous catalytic composition from Experiment 5 and 16.7 g (0.1344 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 250 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 100 g (0.128 mol) of polyorganohydrosiloxane of formula (XVIII) are run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 87.0%. 2 hours after the reactant has been run in, the degree reaches 94.6%, then 95% 8 hours after and 96.2% 24 hours after.

The reaction mass is filtered through sintered glass with a clarcel precoat, Devolatilization is carried out using a rotary evaporator at 100°C under a vacuum of 2 x $10^2$ Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 270 mPa.s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The coloring is 35 hazen units and the platinum content is less than 0.15 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.92.

Turbidity is not observed.

Experiment 7:

0.360 g of heterogeneous catalytic composition comprising 2.5% Pt on a CECA 2S support and 13.9 g (0.112 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 100 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum- The mixture is heated to 90°C. 90 g

(0.107 eq.) of polyorganohydrosiloxane of formula (XVIII) are run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 90.3% and this reaches 99.1% 8 hours later.

After filtration, devolatilization is carried out at 120°C under a vacuum of 2 X $10^2$ Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 320 mPa.s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The coloring is 25 hazen units and the platinum content is less than 0.17 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.96.

No turbidity observed.

Experiment 8:

0.233 g of heterogeneous catalytic composition (5% Pt on a support composed of barium sulphate) from the company Heraeus (100 ppm of Pt in the mixture) and 16.7 g (0.1344 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 250 ml three-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum.

The mixture is heated to 90°C. 100 g (0.128 mol) of polyorganohydrosiloxane of formula (XVIII) are then run in over a period of 3 hours.

After the reactant has been run in, the degree of conversion of SiH is 63.3%. 2 hours after the reactant has been run in, this degree reaches 91.4% and 93.8% 5 hours after the reactant has been run in. 24 hours after, the degree of conversion is 93.1%.

Devolatilization is carried out using a rotary evaporator at 100°C under a pressure of $2 \times 10^{2}$ Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 280 mPa.s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The coloring is 57 hazen units and the platinum content is less than 4.5 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.96.

No turbidity observed.

Experiment 9:

7.78 g of unmilled heterogeneous catalytic composition of CAL 101 type (100 ppm of Pt in the mixture) are introduced into a U-shaped tube equipped with a thermometer and flushing is carried out with argon.

33.4 g of 1,2-epoxy-4-vinylcyclohexane (0.2688 mol, 5% excess) are introduced into a 500 ml three-necked flask connected to the U-shaped tube. The 1,2-epoxy-4-vinylcyclohexane passes into the U-shaped tube containing the catalytic composition (peristaltic pump with rate = 100 ml/min) and then returns to the round-bottomed flask.

The reaction mixture is heated to 90°C. 200 g of polyorganohydrosiloxane of formula (XVIII) are then run into the three-necked flask over a period of 3 hours. The polyorganohydrosiloxane and 1,2-epoxy-4-vinylcyclohexane mixture is subsequently passed over the catalytic composition.

After the reactant has been run in, the degree of conversion of the SiH units is 94.8% and, 2 hours after this, the degree reaches 98.4% to ultimately reach 100%.

The reaction mixture is filtered through sintered glass with a clarcel precoat. Devolatilization is carried out using a rotary evaporator at 100°C under a vacuum of 2 x $10^2$ Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 280 mPa.s. After storing for 3 months (at room temperature and under nitrogen), the viscosity is found to be identical.

The coloring is 114 hazen units and the platinum content is 2.9 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.97.

No turbidity observed.

The catalytic composition is recovered and washed with toluene as soon as the reaction is complete (8 h after the reactant has begun to be run in) and then it is dried with a stream of argon.

Experiment 10:

All the washed and dried heterogeneous catalytic composition of CAL 101 type recovered from Experiment 9 is introduced into a U-shaped tube equipped with a thermometer and then the assembly is conditioned under argon.

33.4 g of 1,2-epoxy-4-vinylcyclohexane (0.2688 mol, 5% excess) are charged to a 500 ml three-necked flask. The 1,2-epoxy-4-vinylcyclohexane is passed over the catalytic composition contained in the U-shaped tube and then returns to the round-bottomed flask (under the action of a peristaltic pump with rate = 100 ml/min).

The reaction mixture is heated to 90°C. 200 g of polyorganohydrosiloxane of formula (XVIII) are subsequently run in over a period of 3 hours. The mixture of polyorganohydrosiloxane of formula (XVIII) and of 1,2-epoxy-4-vinylcyclohexane is subsequently passed over the catalytic composition (under the action of a pump).

After the reactant has been run in, the degree of conversion of the SiH units is 92.4%. 2 hours after this operation of running in the reactant has finished, the degree of conversion is 94.1% and then, 8 hours after, this level reaches 95.4%.

The reaction mass is filtered through sintered glass with a clarcel precoat. Devolatilization is carried out using a rotary evaporator at 100°C under a pressure of 2 x $10^2$ Pa for 2 hours.

A functionalized oil is recovered which has a viscosity of 270 mPa.s. After storing for 3 months (at room temperature and under nitrogen), tho viscosity is found to be identical.

The modified silicone oil obtained is transparent; its coloring is 83 hazen units and the platinum content is 2.1 ppm.

The level of epoxy quantitatively determined/calculated epoxy level ratio is 0.92.

No turbidity observed.

Experiment 11:

2.045 g of heterogeneous catalytic composition comprising 3% Pt on a dried black charcoal support, with the commercial reference 7075 from Engelhard, and 13.46 g (0.108 mol, 5% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a two liter four-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum cap.

The mixture is heated to 100°C. 600 g (0.103 eq.) of polyorganohydrosiloxane of formula (XVI) , in which X = $CH_3$, a = 225 and b = 2, are run in over a period of 2 hours.

After the reactant has been run in, the degree of conversion of SiH is 64.5%. After 23 hours,. it is 83.3%. After heating to 120°C, the degree of conversion of SiH is 100% after 5 days.

After filtration, devolatilization is carried out at 120°C under a vacuum of 1 x $10^2$ Pa for 5 hours.

A functionalized oil is recovered which has a viscosity of 610 mPa.s. This viscosity is found to be unchanged after storing for three months at room temperature under nitrogen.

The coloring is 30 hazen units and the platinum content is less than 0.11 ppm.

Turbidity is not observed.

Experiment 12:

2.55 g of heterogeneous catalytic composition comprising 2.5% Pt on a CECA 2S support comprising 52% by mass of water and 2049 g (16.5 mol, 10% excess) of 1,2-epoxy-4-vinylcyclohexane were introduced under argon into a 3.5 liter reactor equipped with a vertical stirrer, a reflux condenser, a dip pipe, a thermometer and a septum cap.

The mixture is heated to 110°C. 1007 g (15 eq.) of polyorganohydrosiloxane of formula (XVI), in which X = H, a = 1 and b = 0, are run in over a period of five hours via the dip pipe.

After the reactant has been run in, the degree of conversion of SiH is 99.98%.

After filtration, devolatilization is carried out at 120°C under a vacuum of less than 1 x $10^2$ Pa for 10 h.

A functionalized oil is recovered which has a viscosity of 51.3 mPa.s. This viscosity is unchanged after storing for three months at room temperature under nitrogen.

The coloring is 30 hazen units and the platinum content is less than 0.11 ppm.

Turbidity is not observed (0.2 NTU).

Experiment 13:

3.74 g of heterogeneous catalytic composition comprising 2.5% Pt on a dried CECA 2S support and 433.85 g (3.8 mol, 5% excess) of allyl glycidyl ether were introduced under argon into a two liter four-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum cap.

The mixture is heated to 130°C. 500 g (3.62 eq.) of polyorganohydrosiloxane of formula (XVI), in which X = H, a = 9 and b = 4.5, are run in over a period of 5 hours.

After the reactant has been run in, the degree of conversion of SiH is 92.7%. After 10 hours, it is 99.8%.

After filtration, devolatilization is carried out at 120°C under a vacuum of 1 x $10^2$ Pa for 5 hours.

A functionalized oil is recovered which has a viscosity of 62 mPa.s. This viscosity is unchanged after storing for three months at room temperature under nitrogen.

The coloring is 25 hazen units and the platinum content is less than 0.18 ppm.

Turbidity is not observed.

Experiment 14:

3.06 g of heterogeneous catalytic composition comprising 3% Pt on a dried black charcoal support, of reference 7075 from the company Engelhard, 20 g of p-

xylene and 6.74 g (41 mmol, 10% excess) of nadic anhydride were introduced under argon into a 100 ml four-necked flask equipped with a vertical stirrer, a reflux condenser, a thermometer and a septum cap.

The mixture is heated to 120°C. 10 g (37.3 meq.) of polyorganohydrosiloxane of formula (XVI), in which X = $CH_2$, a = 9.1 and b = 4, are run in over a period of two hours.

After 24 hours, the degree of conversion is 41.7% and then 92.4% after 72 hours, 98.9% after 96 hours and 99.7% after 120 hours.

After filtration, devolatilization is carried out, after a temperature rise over two hours, at 120°C under a vacuum of 1 x $10^2$ Pa for 5 hours.

A colorless functionalized oil is recovered.

(7) CONCLUSION

The experiments conducted demonstrate that the polyorganohydrosiloxane of the present invention are different form the starting materials of *Jachmann et al* and due to this difference the hydrosilation reaction of the present invention leads to the production of a silicone that has a stable viscosity and low turbidity.

I further declare that all statements made herein of my own knowledge are true and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001

of Title 18 of the United States Code and that such willful statements may jeopardize the validity of the application or any patent issuing thereon.

Date 2 march 2001

Dr Gerard Mignani

Gérard Mignani